Birdwood kaolinite: a highly ordered kaolinite that is difficult to intercalate- an XRD, SEM and Raman spectroscopic study

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Abstract:

The intercalation of a highly ordered kaolinite from Birdwood, South Australia has been studied using a combination of electron microscopy, X-ray diffraction and Raman microscopy. Highly ordered kaolinites normally intercalate easily and to a high degree. The kaolinite under study was found to intercalate acetamide and formamide with difficulty and more than 18 days were required to achieve more than 20 % intercalation. Further treatment did not improve the degree of intercalation past 60 %. The difficulty of intercalation is attributed to the co-existence of two kaolinite phases, a highly ordered (with a Hinckley index > 1.3) and a highly disordered kaolinite, the latter material appears to coat the highly ordered kaolinite thereby limiting the intercalation. The presence of two forms of silica and a dickite were identified in the sample using X-ray diffraction.

Key Words: acetamide, defect structure, disorder, SEM, formamide, intercalation, kaolinite, Raman spectroscopy, XRD.

1.0 Introduction

Australia has a number of extensive deposits of high-grade kaolinite. Many of these have been the subject of investigation with the aim of commercial development. These include deposits at Weipa and Skardon River in North Queensland, Poochera on the Eyre Peninsula in South Australia, Pittong and Lal-lal in Victoria, Kingaroy in Queensland, and many others. These kaolinites have been formed in a variety of ways and many show unusual behaviour. For example, the Weipa kaolinite consists of small particles with broken edges, has a low crystallinity, and yet has suitable rheological properties for use in paper coating. The Kingaroy deposits are of sedimentary origin and show considerable disorder, yet produces a product with high brightness. Some very highly crystalline kaolinites may be obtained from South Australian deposits, at Mt Hope, Poochera on Eyre Peninsula and at Birdwood near Adelaide.

Kaolinites are often expanded through the insertion of molecules between the layers in a process known as intercalation (Olejnik et al., 1970; Ledoux and White, 1966). Intercalation with dimethylsulphoxide (DMSO) can be used to distinguish different types of clay minerals. For example the DMSO-intercalation of clay mixtures is often used to separate kaolinites from chlorites. The reason why molecules such as DMSO, acetamide, and formamide can expand kaolinite is because the intercalated molecules form stronger hydrogen bonds with the siloxane or gibbsite-like surfaces than those between the (siloxane and gibbsite-like) surfaces in the expanded kaolinite (Cruz et al., 1969; Olejnik et al., 1971; Churchman and Theng, 1984; Thompson and Cuff, 1985; Thompson, 1985;Lipsicas et al. 1986, Raupach et al., 1987, Tunney and Detellier, 1994; Frost et al., 1999). There have been many studies of kaolinite expansion. However studies of their de-intercalation and especially the kinetics of de-intercalation are rare. Further, studies on why some kaolinites will not easily intercalate are even more rare.

Molecules, which may act as both proton donors and acceptors such as urea, hydrazine, formamide, and acetamide normally, intercalate into the kaolinite with ease (Ledoux and White, 1966; Thompson, 1985; Raupach et al., 1987). Such intercalation may be followed by both X-ray diffraction and by a wide variety of

spectroscopic methods. Normally highly ordered kaolinites intercalate easily and disordered kaolinites intercalate with more difficulty (Lipsicas et al., 1986). Birdwood kaolinite is an interesting specimen in that it seems highly ordered and yet apparently intercalates with some difficulty (Kristof et al., 1998).

Raman spectroscopy has proved very useful for determining the molecular structure of intercalated kaolinites (Frost et al., 1998a,b). Infrared spectroscopy has also been successfully used in the past (Ledoux and White, 1966; Raupach et al., 1987). Normally when kaolinites are intercalated with DMSO or potassium acetate additional bands are observed in the Raman spectrum (Frost et al., 1997; Frost and Kristof, 1997; Frost et al., 1998a,b). However, when the inserting molecule does not interact with the hydroxyl sheet changes in the Raman spectra of the intercalated kaolinites are more difficult to observe. Changes can then be observed only by studying the Raman spectrum of the inserted molecule.

The advantages of using Raman spectroscopy are as follows. The method is insensitive to the presence of water, whereas water bands in the hydroxyl-stretching region dominate the infrared spectrum of intercalated kaolinite. Further not all the hydroxyl-stretching bands are observed in the infrared spectrum of kaolinite. The ν_4 band attributed to the in-phase transverse optic mode is not observed. Raman spectroscopy requires no sample preparation, whereas infrared spectroscopy does through either the using pressed pellets or making KBr mixtures for reflectance spectroscopy. We have shown that Raman spectroscopy is more sensitive to changes in the hydroxyl-stretching region. Thus the modification of the kaolinite hydroxyl surface may be studied through the Raman spectra of the hydroxyl deformation and translation modes. It should also be noted that X-ray diffraction determines the extent of expansion of the kaolinite layers through intercalation, whereas vibrational spectroscopy measures the extent of intercalation.

In examining the low defect kaolinites from Poochera and Birdwood we noted that fundamental differences exist between these two materials. The Poochera kaolinite readily forms intercalates with many molecules, whereas the Birdwood kaolinite does not. The Birdwood kaolinite also gels at very low solid loadings, while

the Poochera kaolinite remains fluid at high solids loading. In order to understand why the Birdwood kaolinite is different from many other well-crystalline kaolinites, we investigate the intercalation characteristics of this material, using a combination of X-ray diffraction, electron microscopy and Raman spectroscopy.

2. Materials and Methods

2.1 Geological description

The sample of kaolinite was obtained from a quarry 3 km north of the small South Australian town of Birdwood, 40km north of Adelaide. The main kaolinite workings are confined to a weathered 30m thick, fine-grained mica schist unit at the top of the Saddleworth Formation of Neoproterozoic age. The kaolinite formed by alteration of biotite most likely during the weathering of pyritic, quartz-biotite schist. The age of the deposit is not known but based upon an oxygen isotope value of +13.7% might well be pre-late Mesozoic (Bird and Chivas, 1989). Large patches of very pure kaolin form in fold hinge zones where the quartz content has been reduced either by remobilisation during folding or through leaching by high ground water flows and acidic conditions during weathering (Keeling, 1993). The kaolinite from high-grade zones is well crystallised with a Hinckley index > 1.3 occurring as coarse tight packed crystal stacks in a matrix of fine-grained euhedral kaolinite crystals (Frost and van der Gaast, 1997).

2.2 Kaolinite intercalate preparation

The kaolinite was intercalated by mixing one gram of clay in 25 cm^3 of aqueous acetamide or formamide solution at 25 °C for different periods of time using a magnetic stirrer (Wada, 1961; Weiss et al., 1963 and 1966). The intercalated kaolinite was separated from the solutions by centrifugation, and stored in a desiccator.

2.3 Raman microprobe spectroscopy

In order to collect Raman spectra, a small amount of the kaolinite was placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. No sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge-couple device (CCD). Raman spectra were obtained through excitation with a Spectra-Physics model 127 He-Ne laser (633 nm) and recorded at a resolution of 2 cm^{-1} in approximately 1000 cm^{-1} sections. Repeated acquisitions using the highest magnification, were averaged to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. It should also be noted that the filters in the Renishaw spectrometer start to eliminate the Rayleigh line at about 150 cm^{-1}. This makes the determination of bands below 200 cm^{-1} difficult and unreliable.

Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled selection of the type of fitting, function and allowed specific parameters to be fixed or varied accordingly.

2.4 Scanning electron microscopy (SEM)

SEM studies were carried out using a CanScan FE microscope with a field emission gun operating normally at 20 kV acceleration voltage. The kaolinite particles were coated with gold/palladium films to a thickness of 2-3 nm using a Denton Magnetron Sputter coater system.

2.5 X-Ray Powder Diffraction (XRD)

XRD analysis of the untreated kaolinite was undertaken using the X-ray diffraction facility at the Netherlands Institute for Sea Research, and that of the acetamide and formamide intercalated kaolinites was performed at the Queensland University of Technology XRD facility. XRD analyses on the

untreated material were carried out with a Philips wide angle PW 1050/25 vertical goniometer, equipped with a graphite diffracted beam monochromator. The d-spacing and intensity measurements were improved by application of a self developed computer aided divergence slit system enabling constant area irradiation (20 mm long) at any angle of incidence. The goniometer radius was enlarged from 173 to 204 mm. The radiation applied was CoKα from a long fine focus Co tube, operating at 40 kV and 40 mA. The samples were measured at 50% relative humidity in stepscan mode with steps of 0.02° 2θ and a counting time of 2s. Measured data were corrected with the Lorentz polarisation factor (for oriented specimens) and for their irradiated volume.

Band-fitting of the X-ray data was carried out using a Pearson (IV) function. Fitting was performed by manipulating the raw (unsmoothed/non-filtered) data without any fixation of peak positions or other parameter. Some minor background was removed. A minimum number of Lorentz-Gauss cross-product function bands was used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results with $r^2 > 0.995$ were obtained.

3. Results and Discussion

3.1 Raman spectroscopy of the intercalated kaolinites

The band component analysis of the kaolinite, its acetamide intercalate and the formamide intercalate are shown in Fig 1. The results of the analyses are reported in Table 1. The Raman spectrum of the untreated Birdwood kaolinite shows bands at 3693, 3684, 3670, 3651 and 3620 cm^{-1} with relative intensities of 34.0, 16.6, 7.6, 12.6 and 28.6 %. This kaolinite is highly ordered, not only as evidenced by the Hinckley index but also by the ratio of the two in-phase hydroxyl stretching bands at 3693 and 3684 cm^{-1}. This ratio has been used as a guide for the determination of kaolinite order and disorder (Frost and van der Gaast, 1997; Frost et al., 1999). When the kaolinite is intercalated with acetamide no additional bands are observed (Figure 1b). Bands are observed at 3693, 3683, 3670, 3653 and 3620 cm^{-1} with relative intensities of 34.0, 7.5, 2.1, 2.9 and 53.4%.

The only evidence that some changes in the structure of the kaolinite, as a result of intercalation has occurred is in the decrease in relative intensities of the ν_1 and ν_4 bands in the Raman spectrum (Frost and van der Gaast, 1997; Frost et al., 1999 a, b, c). The ν_4 band has diminished in intensity from 16.6 to 7.5 %. The decrease in intensity of these bands is attributed to the interaction of the inner surface hydroxyls with acetamide. The decrease in intensity may be used to measure the extent of intercalation (Frost et al., 1998b). Comparison of the Raman spectra in Figures 1a and b shows this decrease in intensity. Some changes in the profile of the ν_4 band are also observed. However no additional hydroxyl bands are observed. This makes the observation of intercalation of kaolinites with acetamide through Raman spectroscopy quite difficult. Some perturbation of the inner surface hydroxyl stretching bands is observed, consistent with previously published data (Raupach, 1988)

When the kaolinite is intercalated with formamide (Figure 1c), an additional band at 3627 cm^{-1} is observed which is attributed to the interaction of the amide group with the inner surface hydroxyl groups. The band makes up 11.2 % of the total relative intensity. Bands are observed at 3693, 3683, 3671, and 3651 cm^{-1}. The relative intensities of these bands are 37.2, 11.7, 6.6, 4.0, and 29.2 %. The relative intensity of the ν_1 band has remained the same. The ν_4 band has decreased slightly in relative intensity. Some relative intensity decrease in the ν_2 and ν_3 bands is also noted. Thus as in this case of the Raman spectrum of acetamide intercalated kaolinite, changes in the Raman spectrum of the hydroxyl stretching region of the formamide intercalated kaolinite are small. The difficulty in using the Raman spectra is to know whether the kaolinite has been intercalated. The XRD results compliment the Raman spectroscopic data and provide information on the extent or degree of expansion of the kaolinite layers through intercalation of this kaolinite with acetamide and formamide. Further the ability of Raman spectroscopy to determine disordered phases is not good. The Raman spectrum only shows the occurrence of the highly ordered phase and not that of any disordered phase. Such disordered phases are better determined by infrared and solid state NMR spectroscopy (Raupach et al., 1987; Raupach, 1988, Frost et al., 1999b).

3.2 XRD of the intercalated Birdwood kaolinite

The intercalation of the Birdwood kaolinite with acetamide and formamide is evidenced by the presence of the (001) reflection with a d-spacing of 10.9 Å, representing the expanded phase. Figures 2 and 3 show the XRD patterns for different time intervals. The analyses of the 001 d-spacings are reported in Table 2. The kinetics of intercalation are shown in Figure 4. Twenty days are required to achieve > 50 % intercalation. No significant increase in intercalation occurs after this period. The rate curves are typically S shaped as reported by Raussell-Colom and Serratosa (1987). The intercalation starts off slowly and remains at a low level up to 15 days. The greatest increase occurs between 15 and 20 days and reaches a maximum around the 60 % level. The intercalation then stops. The intercalation process appears to involve two time sequences (a) 0-5 days and (b) 5-15 days. An initial start-up time occurs before substantial intercalation occurs. Other kaolinites such as the Poochera material with a Hinckley index of 1.35 shows 95% intercalation. The question arises as to why the Birdwood kaolinite cannot be intercalated in excess of this 60 % level.

3.3 SEM

Figures 5a, 5b and 5c show SEM images of the Birdwood kaolinite. Figure 5a clearly shows kaolinite books of varying sizes with low aspect (crystal-width to thickness) ratios. Individual platelets are noticeable. Some pseudohexagonal edges on kaolinite platelets are observed. Some of the kaolinite particles are rolled and some have rough edges (Figure 5b). The surfaces of the kaolinite flakes show that they are a composite of smaller particles <300nm across (Figure 5c). The rolled particles are not considered to be the halloysite polytype as there is no infrared evidence for the presence of halloysite, although this would depend on the concentration and hydration of the halloysite present. Rather, the rolled particles are indicative of the disordered kaolinite and the thinness of the kaolinite flakes.

The particles of the Birdwood kaolinite are mostly below 500 nm in size, forming books (vertical stacks) and individual flakes. Some of the stacks show remnants of euhedral developed edges but most are somewhat ragged. This suggests

that some dissolution has taken place. The basal surfaces of these stacks are rough and give the appearance of degradation from an interlocking mosaic of kaolin "crystallites". Small individual platelets (below 100 nm in diameter) are the cause of this decay and they also differ in morphology. Some of them display the pseudo-hexagonal shape but others are irregular, both very thin, some rolling into tubes. Some colloidal particles may be present on the platelet boundaries.

3.4 XRD of the untreated kaolinite

X-ray diffraction of the Birdwood kaolinite shows a strong asymmetry on the low angle side of the 001 peak (Figure 6). Due to the axial divergence aberration peaks at these low angles tend to show this shape (Klug and Alexander, 1974). Peaks of this width normally can be fitted with a single Pearson IV peak. Here, however, the fitting was poor, especially on the low angle side. After introducing a second peak of the same type a good fit was obtained with $r^2 = 0.9995$. We suggest that two phases are present in the Birdwood kaolinite. For the hk region in the XRD pattern the same situation arose; a reasonable fit could be obtained only after introducing a second peak for every major kaolinite peak. At 2-theta angles of about 24 and 29°, however, some "background" was left after fitting. Introducing two broad peaks the fitting showed that one was centred at 4.00 Å (Band I) and one at 3.62 Å (Band II). Band I probably represents pure to almost pure but poorly crystalline SiO_2, for which a band normally is found at 4.04 to 4.09Å, whilst band II may be due to poorly crystalline SiO_2, of which the Si atoms are partly replaced by other atoms, probably Al. van Bennekom et al. (1989) found 6 to 7% Al replacing Si atoms in biogenic silica in deep sediments from the Angola Basin, causing the band of poorly crystalline silica to shift towards 3.64 Å in their XRD patterns. This agrees well with the d-value found for Band II. We can conclude from band II that Al has replaced Si in the poorly crystalline Birdwood material. Additionally, a dickite reflection $(11\ \overline{2})$ at 4.141 Å is observed. The reflection at 3.531 Å is ascribed to anatase. The presence of these poorly crystalline materials may contribute to the gelling properties of the Birdwood kaolinite.

Figure 7 shows the band component analysis of the (hk0) reflections. The Birdwood kaolinite gives sharp hk reflections, but by fitting the area between 22 and 35 degrees, two patterns can be observed, thus suggesting two types of kaolinites. On the high angle side of the sharp hk reflections, broad asymmetry is observed. These hk reflections are always asymmetric towards the high angle side because of turbostratic ordering. In other words the more random the stacking, the greater the asymmetry that is observed. In the determination of crystallinity, the sharpest peaks are used and the crystallinity index deduced. The poorly crystalline kaolinite is overlooked in such a method. Some low intensity reflections are also observed and are attributed to dickite. A broad band centred at 3.8 Å, which indicates an amorphous compound, and a broad weak band centred at 14.0 Å are also observed. Thus it is concluded that the two types of kaolinite are intimately intergrown in such a way that that the well crystallised kaolinite may be prevented from intercalation by the intergrowth material. Namely the broad band at 3.8 Å is indicative of intergrowth areas (domain borders). Because of this intergrowth some misfits between the layers may be observed and this is indicated by the 14 Å reflection.

The results of the XRD analyses are reported in Table 3. The two groups in the table, A and B, each represent a kaolinite; A is the well crystallised kaolinite and B the poorly crystallised one. Band component analysis of the 001 peak shows two 001 spacings at 7.17 Å and 7.23 Å. The relative intensities of these two peaks are 49.5 and 50.5 %. The peak width of the 001 d-spacings is 0.186 for the 7.17 Å kaolinite and 0.5728 for the 7.23 Å kaolinite respectively. The width of the 7.23 Å kaolinite d-spacing is three times that of the highly ordered kaolinite, thus indicating a very disordered kaolinite. As with the (001) peak, the (002) reflection also consists of two peaks. The ratio of intensities seems to differ, probably because the structure factor for both kaolinites is different.

Among kaolinite peaks from series B, I and II are strongly asymmetric towards the high angle side. It is clear that there is a mixture of a highly ordered kaolinite and a disordered kaolinite. Moreover, this material is admixed with some dickite. Only one dickite peak (11 $\overline{2}$) is observed, although 6 more should be present at angles up to the (002) reflection. But they are probably too weak to be seen and in

some cases are strongly overlapped by kaolinite peaks. Moreover the material contains some poorly crystalline materials: B1 (Table 1) represents almost pure but poorly crystalline SiO_2. This band is at 4.00 Å. Pure silica gives a spacing of 4.04 to 4.09 Å. B2 represents a poorly crystalline silica with incorporation of an ion that can replace Si and contract the structure. It is apparent that this must be Al. Band I from the almost pure silica, belongs to the colloidal, unfixed grains, in the SEM pictures. Band II from the silica with aluminium substitution, could be the material at the edges of the kaolinite plates. This means that we have: dickite, kaolinite A, kaolinite B, Al-substituted silica, and silica.

3.5 Genesis of Birdwood kaolinite

Both the XRD patterns and the SEM pictures show that the Birdwood kaolinite consists of a mixture of a highly ordered kaolinite and a disordered kaolinite. It is probable that the highly ordered phase intercalates readily but the highly disordered kaolinite does not. The fact that the disordered kaolinite coats the ordered kaolinite explains why this particular kaolinite takes so long to intercalate. It appears that after formation of the well crystalline kaolinite, there has been a process of dissolution and precipitation that has altered a part of the original kaolinite into a poorly crystallised one. The two peaks in the 001 d-spacing evidence this. Moreover, the poorly crystalline kaolinite has probably formed at the edges of the original particles preventing intercalation.

The question arises as to how the poorly crystallised kaolinite has been formed in this material;

(a) has a part of the well-crystallised kaolinite been dissolved and precipitated as a poorly crystallised kaolinite? or,

(b) has a part of the well-crystallised kaolinite been directly transformed into a poorly crystallised material and have the colloidal particles (amorphous in this case) been formed in successive acid attack of the poorly crystallised kaolinite?

(c) Another means of formation of the two strongly related types of kaolinite is that first an amount of well-crystallised kaolinite is developed under perfect conditions for crystallisation.

If the first case is true, it is not understood why the poorly crystallised kaolinite precipitates again. It can be imagined is that the atoms of the well crystallised kaolinite have been dissolved row by row and precipitated as a poorly crystallised kaolinite because of the presence of some other factor. But what would happen with the next rows of atoms from the well crystallised kaolinite? They should be shielded by the newly formed kaolinite. This shielding would affect the kinetics of intercalation. If the second case is true, then this may explain why dickite is sometimes formed in the middle of kaolinite booklets.

In a second stage the ratio of Si: Al changed so that at this second stage the poorly crystallised kaolinite developed on the crystal matrix of the well-crystallised kaolinite thus blocking the interlayer space for intercalation. Small colloidal particles could have developed in a third stage when the Si :Al ratio changed again thus giving rise to particles with structureless edges and separately developed colloidal particles.

4. Conclusions

This research has focussed on the reasons why a particular Australian kaolinite has been found difficult to intercalate. The material expands slowly with acetamide and formamide, requiring some 18 days or more to reach 20 % intercalation. Even after prolonged stirring, only 60 % of the kaolinite could be intercalated. Even with further thermal treatment and stirring, this degree of intercalation could not be increased. Raman spectra showed very little difference between the sample that had been treated for 20 days and the untreated kaolinite.

The reason why this kaolinite from Birdwood is difficult to intercalate is attributed to the presence of a highly disordered kaolinite, coating the surface of a highly ordered phase of the clay. This together with the presence at the surface of some siliceous colloidal material prevent the penetration of all of the kaolinite layers by the inserting molecule. The maximum extent of intercalation (60 %) probably represents the minimum concentration of highly ordered kaolinite present in the sample.

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Table 1 Results of the band component analysis of the hydroxyl-stretching region of the Raman spectrum of Birdwood kaolinite.

Sample	Band centre/ cm^{-1}	Band Widths/ cm^{-1}	%area
Raman spectrum of the hydroxyl stretching region of the untreated kaolinite			
ν_1	3693	13.2	34
ν_4	3684	13.4	16.6
ν_2	3670	15.3	7.6
ν_3	3651	17.3	12.6
ν_5	3620	5.6	28.6
Raman spectrum of the hydroxyl stretching region of kaolinite intercalated with acetamide			
ν_1	3693	11.4	34.0
ν_4	3683	18.5	7.5
ν_2	3670	10.0	2.1
ν_3	3653	12.0	2.9
ν_5	3620	7.3	53.4
ν_6			
Raman spectrum of the hydroxyl stretching region of kaolinite intercalated with formamide			
ν_1	3693	15.2	37.2
ν_4	3683	10.3	11.7
ν_2	3671	18.2	6.6
ν_3	3651	11.2	4.0
ν_5	3620	5.6	29.2
ν_6	3627	4.0	11.2

Table 2 Percentage intercalation of Birdwood kaolinite with acetamide and formamide

Time/days	001 d-spacing of untreated kaolinite	001 d-spacing of acetamide intercalated kaolinite	001 d-spacing of formamide intercalated kaolinite	% Intercalation with acetamide	% Intercalation with formamide
0.5	7.14	10.74	10.9	3.50	3.75
1	7.14	10.80	10.9	5.55	7.78
5	7.14	10.88	10.9	12.6	19.4
10	7.14	10.90	10.9	15.5	26.3
15	7.14	10.90	10.9	20.5	34.2
20	7.14	10.90	10.9	56.0	58.6
30	7.14	10.90	10.9	57.0	59.5
50	7.14	10.90	10.9	58.0	60.5

Table 3 Table of XRD parameters for Birdwood kaolinite

A	D (Å)	hkl	Width (º2θ)	**B**	D (Å)	hkl	Width (º2θ)
I	4.479	020	0.20		4.467	020	0.69
II	4.372	$1\bar{1}0$	0.18		4.369	$1\bar{1}0$	0.85
III	4.191	$11\bar{1}$	0.23	2	4.203	$11\bar{1}$	1.04
IV	3.850	$02\bar{1}$	0.20	$\bar{2}$	3.869	$02\bar{1}$	0.33
V	3.746	021	0.24		3.760	021	0.21
VI	3.583	002	0.21		3.592	002	0.41
VII	3.382	111	0.26		3.400	111	0.94
VIII	3.157	$11\bar{2}$	0.23		3.169	$11\bar{2}$	0.31
IX	3.110	$\bar{1}\bar{1}2$	0.21		3.127	$\bar{1}\bar{1}2$	0.21
B1	4.00		2.27				
B2	3.62		2.39				
Dickite	4.141	$11\bar{2}$	0.21				
Anatase	3.531						

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